Sizing effect on reclaimed continuous carbon fibres's properties extracted from recycled automotive composite parts

SIZING EFFECT ON RECLAIMED CONTINUOUS CARBON FIBRES' PROPERTIES EXTRACTED FROM RECYCLED AUTOMOTIVE COMPOSITE PARTS

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Abstract

The growing need for recycling carbon fibre reinforced polymers (CFRPs) is driven by increasing environmental sustainability concerns. CFRPs, valued for their strength-to-weight ratio and corrosion resistance, are extensively used across various industries, leading to significant waste accumulation and environmental impact. Maintaining the mechanical performance of carbon fibres, the primary reinforcement in CFRPs, is crucial for the structural integrity and functionality of recycled materials. Chemical and mechanical recycling methods offer promising approaches for fibre reclamation, each with its benefits and drawbacks. As recycling efforts progress, robust characterization methods are essential to assess the integrity and quality of recycled fibres accurately. A novel optical method presented in this study offers a framework for evaluating fibre filament loss during recycling, providing valuable insights into the effectiveness of recycling initiatives. Tensile tests further demonstrate that while recycled fibres exhibit decreased properties compared to reference fibres, sizing significantly enhances the tensile strength of recycled fibres, underscoring the importance of appropriate treatment methods in improving the performance of recycled materials for composite applications.

1. Introduction

The necessity of recycling carbon fibre reinforced polymers, or CFRPs, has increased more and more in recent years as environmental sustainability concerns have grown. Because of its remarkable strength-to-weight ratio and resistance to corrosion, CFRPs have gained value as materials in a number of industries, including construction, automotive, and aerospace. Due to their extensive use, the amount of wastes has increased quickly, creating serious disposal problems as well as negative environmental effects. The main reinforcement of composites, carbon fibres, provide exceptional mechanical performance which is essential to the structural integrity and functionality of the structure. Therefore, in order to maintain the functional and economic viability of recycled CFRPs, these values must be maintained throughout the recycling process. There are numerous obstacles in the way of recycling CFRPs, necessitating solutions that create balance between material performance and environmental responsibility [1].

The scientific community (as well as industry) has found great appeal in two methodologies: chemical and mechanical recycling, as these are workable approaches for fibre reclamation. Whereas mechanical recycling shreds and with a sorting method separates fibres from the matrix (or uses the aggregates as fillers), chemical recycling breaks down the polymer matrix to remove carbon fibres. Both approaches have unique benefits and drawbacks, so it's important to consider their consequences carefully when preserving fibre qualities [2].

As CFRP recycling progresses, robust characterisation methods that measure the integrity and quality of recycled fibres are also being developed. The quantity of fibre loss and degradation during recycling is frequently not adequately assessed by conventional methods, which hinders optimization efforts and increases the amount of recovered materials used. Novel characterisation techniques that offer data on physical attributes, such as fibre morphology, distribution and breakage after recycling, are thus needed. This work emphasizes the importance of a novel optical method designed to accurately measure fibre filament loss during recycling. Utilizing optical imaging and analysis methods, this approach provides

a framework for assessing the effectiveness of recycling initiatives. Tensile tests of the recycled and sized fibres have been performed to assess the effect of recycling and sizing process on fibre properties [3].

2. Experimental

2.1 Materials & Methods

In this work, Tenax – E STS40 E23 24k carbon fibres have been used from Teijin Limited (Japan). The same, recycled, carbon fibres have been supplied by University of Patras or Silesian University of Technology, derived from a solvent based solvolysis process [4] and plasma assisted solvolysis process [5]. Commercial sizing solution, Hydrosize® HP2-06 (Michelman, Belgium) was used to size the CFs. HP2-06 is an anionic/nonionic phenoxy aqueous dispersion designed for use as a fibre sizing agent that enhances compatibility between fibres and matrix, resulting in better mechanical performance of composites. Fibre's surface morphology was assessed with a Hitachi TM3030Plus (Japan) tabletop SEM system using 15kV and the secondary electrons detector. Thermogravimetric analysis was performed to assess if there is resin residue on the fibre surface after recycling process, using a TGA apparatus (STA 449 F5 Jupiter, Germany). Instrument calibration for temperature and sensitivity was performed prior to testing. Tests were performed with ~20 mg of carbon fibres at a heating rate of 20 °C/min in N_2 atmosphere (50 mL/min), and mass change was measured as a function of temperature. The analysis was performed in accordance with ISO 11358. A 2-part resin system Epoxidharz and Harter W300 from Faserverbundwerkstoffe (Germany) has been utilized to produce samples for optical microscopy analysis and to produce the impregnated samples for tensile tests. The tensile strength test was performed according to ASTM D 4018. The used specimens were tabbed resin-impregnated and consolidated fibre bundles. A universal tensile machine TE Forcespeed/Jinan WDW Series (China) was used with a load cell of 5kN.

To calculate tensile strength the following formulas were used:

$$MUL = \frac{W_1}{\mathrm{L}} \quad (1)$$

MUL: mass per unit length (g/m), W_1: mass of the specimen (g), L: length of the specimen (m)

$$UTS = P * \frac{\rho_f}{MUL} \quad (2)$$

UTS: ultimate tensile strength (MPa), P: maximum load measured in tensile test (N), ρ_f: fibre density (g/cm^3), MUL: mass per unit length (g/m)

2.2 Sample preparation for optical analysis

In optical microscopy, achieving high-quality results relies primarily on thorough sample preparation, with an emphasis on obtaining an excellent surface finish. The quality of the surface finish significantly influences the clarity and detail captured by the microscope. Imperfections, height difference, curved surface, irregularities, or contaminants on the sample surface can obscure or distort the image, undermining the accuracy and reliability of the analysis.

In our procedure, carbon fibres needed to be aligned vertically within a disk-shaped mold and impregnated with resin to ensure that the fibres remained in this vertical position during resin curing. To achieve this, the fibres were initially placed under tension on a metallic plate, and resin droplets were applied to their surface using a pipette. The specimens were then allowed to cure in an oven at 50°C for 24 hours. Subsequently, the fibre-impregnated bundles were cut into 1 cm pieces and placed inside 30 mm diameter cylindrical molds equipped with a metal fixture to secure the samples in a vertical position. Five samples were introduced per mold, and epoxy resin was then poured in. The specimens were left to cure for an additional 24 hours in the oven at 50°C. The disk-shaped specimens were then removed from the mold to proceed with the grinding process. Grinding /polishing of samples included the following 6 grinding and 2 polishing steps:

Table 1. Grinding parameters

Paper type	Suspension type	Force (N)	Turns per minute	Time (min)
SiC 220	Water	5	300	0.5

SiC 220	Water	10	300	0.5
SiC 500	Water	10	300	0.5
SiC 1200	Water	10	300	0.5
SiC 2200	Water	10	300	0.5
SiC 4000	Water	10	300	1

Table 2. Polishing parameters

Paper type	Suspension type	Force (N)	Turns per minute	Time (min)
MD- Largo	DiaPro Largo 3µm	10	150	5
MD- Dur	DiaPro Nap 1µm	10	150	5

3. Results

3.1 Surface morphology – SEM

The surface morphology of CFs is examined in Figure 1. In Figure 1a, the smooth, rigid surface of reference CF is depicted. Similarly, Figure 1c illustrates a comparable morphology, where the recycled fibres from plasma-assisted solvolysis are displayed. Here, all the resin has been effectively removed, leaving behind clean fibres ready for reuse. In contrast, the matrix from solvent solvolysis hasn't been entirely eliminated, as significant quantities of resin residue are evident on the surface of CFs. This could potentially have a detrimental effect, as it may significantly affect wettability during resin impregnation for the preparation of new composites. This difference is evident in their respective sized versions, depicted in Figure 1d for solvent solvolysis, where resin residues remain on the fibre surface, resulting in irregularities in morphology. Finally, in Figure 1e, representing plasma-assisted solvolysis, a smooth fibre surface is exhibited.

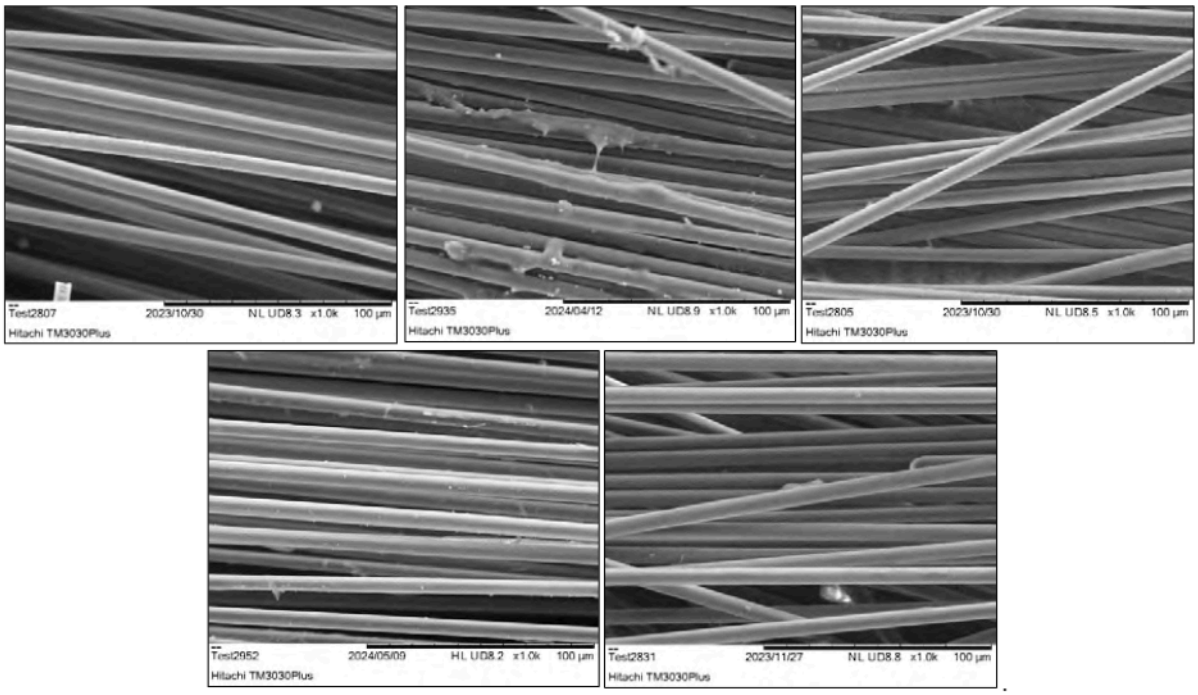


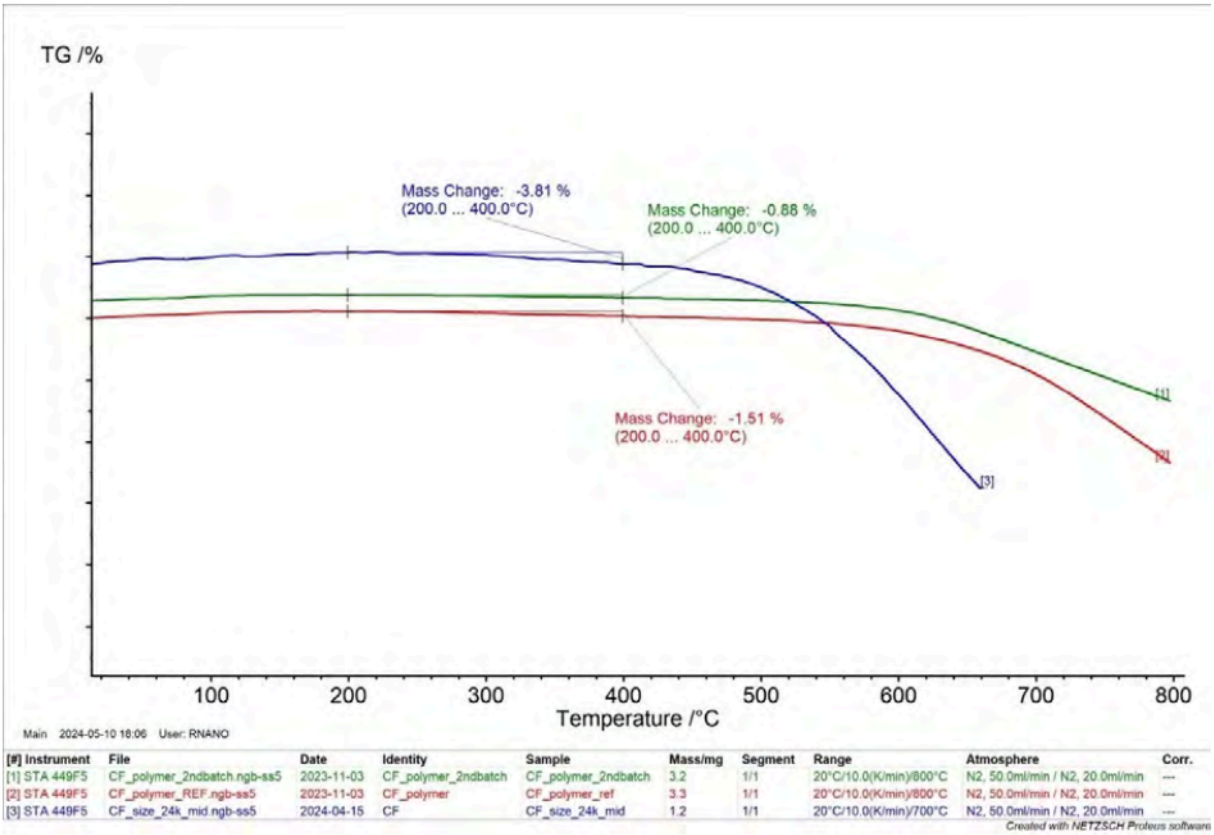
Figure 1. SEM images of (a) reference CFs, (b) recycled with solvent solvolysis (c) recycled with plasma solvolysis, (d) sized recycled from solvent solvolysis and (e) sized recycled from plasma solvolysis

3.2 Thermogravimetric analysis

The thermal behavior of fibres is analyzed using thermogravimetric analysis. Reference, solvent-solvolysed, and plasma-assisted solvolysed fibres are presented in a single graph to facilitate comparison (Figure 2). The first area of interest spans the temperature range of 200 to 400°C, where polymer degradation occurs. In cases where differences in mass change are minimal, deriving solid quantitative conclusions can be quite challenging. In such instances, the graphical form becomes crucial, as it

provides all necessary information. As observed in the temperature range of 200 to 400°C for the reference fibres (red line), there is a notable change in the graph's shape, a sharp decline (at 300 °C) attributed to decomposition, evaporation, or other chemical reactions, in this case, decomposition of the pre-existing commercial sizing. Conversely, for plasma-assisted solvolysed fibres (green line), no similar phenomenon is evident; instead, there is only negligible mass loss over time, indicating complete resin removal during the solvolysis process, consistent with SEM analysis findings. However, a nearly 4% mass loss in the solvent-solvolysed fibres (blue line) suggests the presence of residual resin on the fibre surface.

Most notably, a significant drop in mass for solvent-solvolysed fibres starts at 500°C, attributed to fibre decomposition. This is a significant deviation, as neither reference fibres nor plasma-solvolysed fibres undergo decomposition before 650°C, indicating that the solvent solvolysis process has compromised the structural integrity of the fibre, likely by damaging the graphitic structure. This deterioration suggests that the intensity of the solvent solvolysis process negatively impacts fibre properties, rendering the parameters that the process has been performed less efficiently.



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 449F5	CF_polymer_2ndbatch.ngb-ss5	2023-11-03	CF_polymer_2ndbatch	CF_polymer_2ndbatch	3.2	1/1	20°C/10.0(K/min)/800°C	N2, 50.0ml/min / N2, 20.0ml/min	---
[2] STA 449F5	CF_polymer_REF.ngb-ss5	2023-11-03	CF_polymer	CF_polymer_ref	3.3	1/1	20°C/10.0(K/min)/800°C	N2, 50.0ml/min / N2, 20.0ml/min	---
[3] STA 449F5	CF_size_24k_mid.ngb-ss5	2024-04-15	CF	CF_size_24k_mid	1.2	1/1	20°C/10.0(K/min)/700°C	N2, 50.0ml/min / N2, 20.0ml/min	---

Figure 2. TGA graphs for reference fibres (red line), solvent solvolysed fibres (blue line) and plasma assisted solvolysed fibres (green line). The Y-axis represents weight loss (each bar represents a 20% loss), while the X-axis indicates temperature.

3.3 Optical microscopy analysis

Polished samples as prepared in Section 2.2 were placed under an Olympus BX53M microscope using a brightfield observation method, with a camera resolution of 5760 x 3600 pixels. The Olympus Stream Motion software was used for capturing and analyzing images. Panorama feature was utilized to stitch together multiple images into one, facilitating the analysis of the samples.

Figures 3-5 illustrate the various materials utilized in this study. The epoxy matrix used during the preparation of the disk specimens is represented in light grey. Air holes trapped within the impregnated fibre bundles are indicated in black to signify the absence of material. Carbon fibres are depicted in white. Contrary to the samples crafted with reference fibres, both recycled refined and recycled fibre specimens exhibit a black coloration surrounding the fibres, which could compromise the analysis

(refined fibre samples were identical to recycled ones, with the addition of an extra combing step aimed at removing broken filaments). This is attributed to insufficient time for the specimens to achieve a uniformly polished surface. Plasma-assisted solvolysed fibres were chosen as recycled fibres for this analysis since results from TGA and SEM were more promising for this case with current process parameters. Despite the higher quality of the reference samples compared to the recycled ones, they also displayed black areas along the perimeter of the disk, indicating that the middle part of the sample is more homogeneous than the edges (the force from the machine during polishing is applied in the disk centre). Consequently, all three samples underwent an additional polishing step for 10 minutes using a 1μm suspension to address this issue. A quick observation with the microscope confirmed that this was adequate for the reference samples, whereas the recycled samples required an additional 7 minutes of polishing. Results are depicted in the following images.

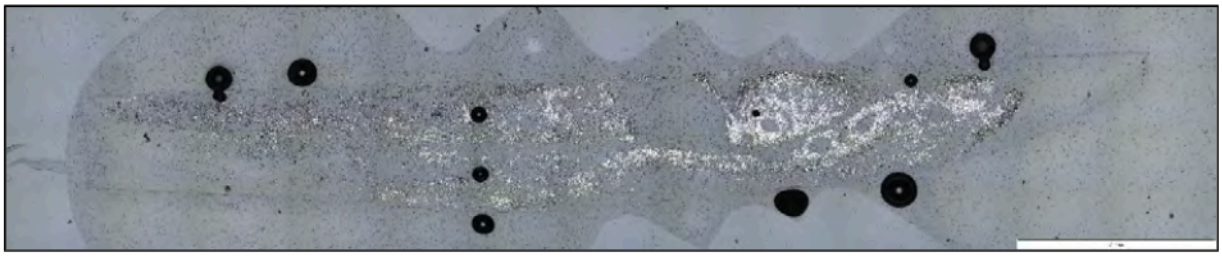


Figure 3. Reference fibre sample

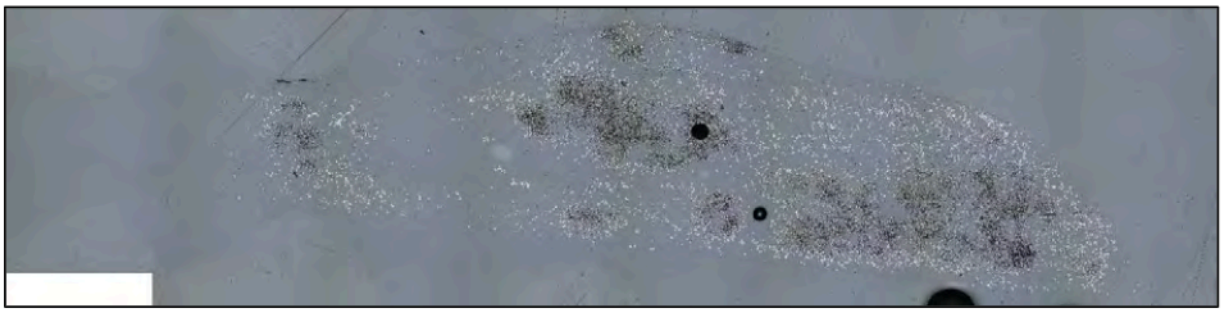


Figure 4. Plasma-assisted recycled fibre sample

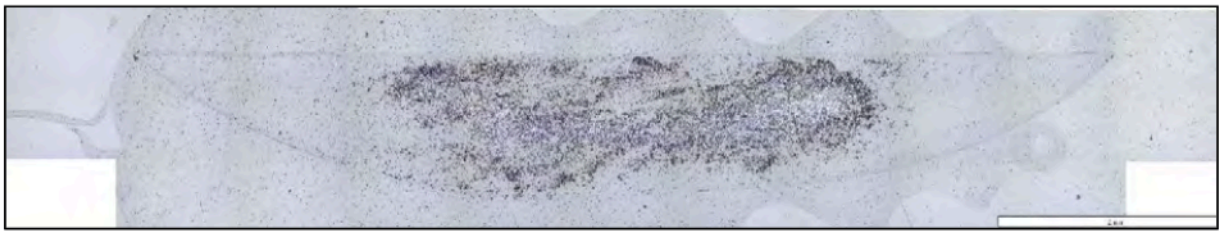


Figure 5. Plasma-assisted recycled refined fibre sample

Reference samples appear flawless, while those derived from recycled fibres have also seen significant enhancement, although occasional dark areas remain. It was noted during the analysis that additional polishing may not necessarily improve the depiction, as recycled fibres are inherently more fragile than their original, resulting in a less smooth surface regardless of polishing duration. Nevertheless, these conditions suffice for further analysis aimed at quantifying the filament count across all samples. This will be performed through three different validation methods: firstly, using the segmentation software tool within the Olympus software; secondly, employing a python algorithm for fibre counting; and lastly, utilizing a plug-in for particles counting within the ImageJ software.
Filament count is presented in the following table, with the analysis of the results in the following chapters:

Table 3. Filament count master table

Reference	Recycled Refined	Recycled

# Sample	Python	ImageJ	Microscope Software	Python	ImageJ	Microscope Software	Python	ImageJ	Microscope Software
1	24328	22145	15916	15260	13059	14460	14796	15626	11496
2	24358	24601	15476	15398	12470	14044	15921	15752	13393
3	22512	22444	12616	15663	13166	14648	16448	15851	15465
4	23239	25401	15234	15636	13379	15127	16176	15348	14884
5	24190	23907	15040	16825	12235	15464	17039	14948	14390
AVG	**23725**	**23700**	**14856**	**15756**	**12862**	**14749**	**16076**	**15505**	**13926**
STDEV	**820**	**1391**	**1294**	**620**	**486**	**558**	**827**	**364**	**1556**
error (%)	**3.5**	**5.9**	**8.7**	**3.9**	**3.8**	**3.8**	**5.1**	**2.3**	**11.2**

ImageJ analysis

Analyzing images with ImageJ for fibre quantification involves several sequential steps. Initially, the chosen image is imported into the software and converted to an 8-bit format, transitioning it to grayscale. Subsequently, the 'Brightness/Contrast' tool is utilized, accessed through 'Image' followed by 'Adjust', enabling adjustments to enhance the visibility of the fibres. Typically, this involves increasing the contrast and reducing brightness until the fibres appear as white against a black background, facilitating clearer discrimination. Following this enhancement, the image is subjected to binarization via the 'Make Binary' function under 'Process', converting it into a black-and-white representation based on a threshold value. Then, the 'Watershed' algorithm is applied to segment overlapping or adjacent fibres accurately. Once the image is appropriately processed, the 'Analyze Particles' function is invoked, initiating a new window where parameters such as circularity and size can be set to filter out artifacts or irrelevant features. Finally, upon executing the analysis, ImageJ computes the number of fibres present in the image based on the specified criteria, providing quantitative data crucial for assessing the fibre distribution within the resin cross-section. An indicative example after image analysis can be found in Figure 6.

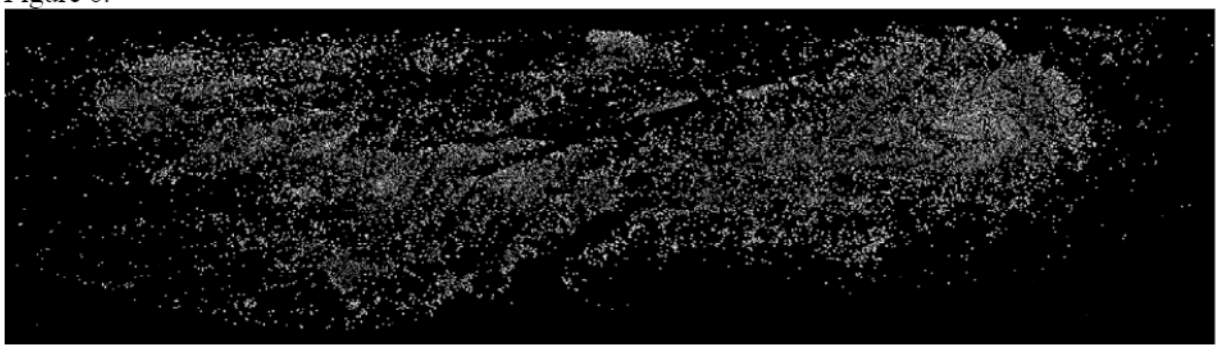


Figure 6. Counting of recycled CFs through ImageJ software

Python script

This Python script automates the analysis of images to quantify the fibre volume fraction, similar to the process conducted with ImageJ. Initially, the script imports necessary libraries and sets up an Excel workbook to record the results. The images are loaded from a specified directory, and a loop iterates over different threshold values to distinguish fibres from the background. For each threshold, the image is converted to grayscale, and a binary thresholding technique is applied to isolate light-colored regions presumed to be fibres. Contours of these regions are then identified, drawn onto the original image, and saved for visual inspection. Simultaneously, the script records the file name and the count of identified fibres into an Excel file. Moreover, it calculates the fibre volume fraction by dividing the total area occupied by fibres by the total area of the image. This metric provides quantitative insight into the proportion of fibres within the resin cross-section. The script ensures systematic analysis and data recording, facilitating efficient and reproducible assessment of fibre distribution in materials science applications.

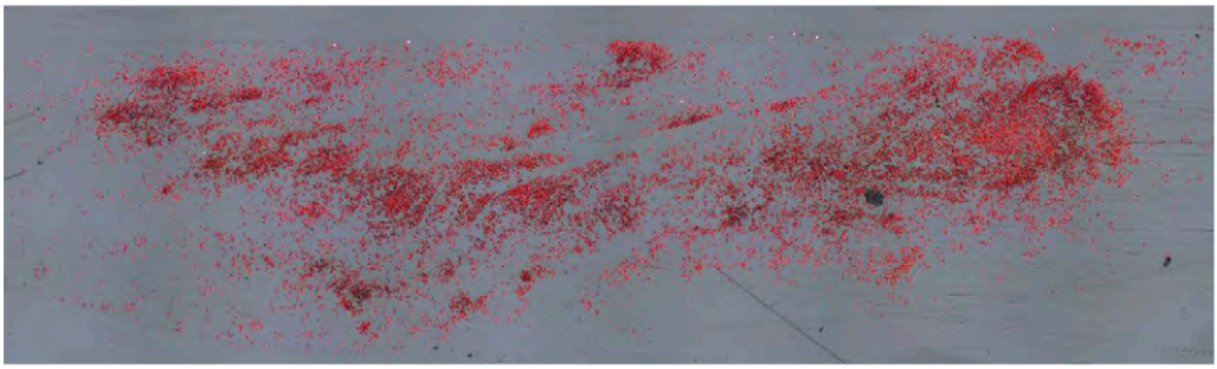


Figure 7. Counting of recycled CFs through Python

Olympus software analysis

The fibre analysis using Olympus software began by importing optical microscopy images captured with the Olympus microscope. Within the software, image enhancement tools were utilized, with brightness and contrast being adjusted to optimize fibre visibility against the background. Subsequently, semi-automated methods provided by the software were employed to identify and count fibres. These methods utilized customizable algorithms to segment fibres based on their color, intensity and texture characteristics. Once fibres were accurately identified, the amount of fibres was calculated.

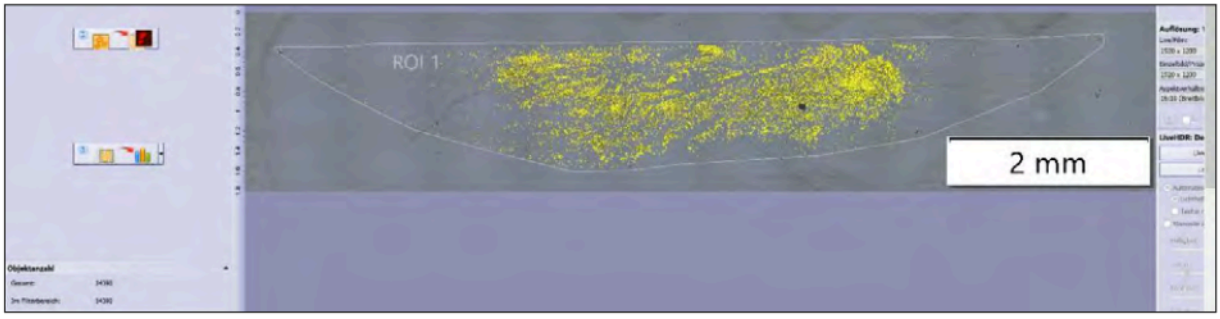


Figure 8. Counting of recycled CFs through Olympus software

3.4 Tensile properties

Tensile tests were conducted on reference fibres, recycled fibres from plasma assisted solvolysis (chosen for their promising results from TGA and SEM analyses), and sized recycled fibres. As expected with recycled fibres, both the sized and unsized recycled fibres exhibited decreases in tensile properties compared to the reference fibres. However, the sized recycled fibres showed a relatively better performance in terms of tensile strength. Despite filament damage and the reduction in filament count, the sized recycled fibres exhibited only a 10% decrease in tensile strength compared to the reference fibres. This decrease can be attributed to the effects of the recycling process and potential alterations in fibre properties. However, the application of sizing to the recycled fibres appeared to mitigate some of these negative effects, resulting in improved tensile strength compared to the unsized fibres. Conversely, the unsized fibres demonstrated a more significant decrease in tensile strength, approximately 22% less than the reference fibres. This reduction can be expected due to factors such as irregularities in fibre morphology, poor fibre alignment within the matrix, weak interfacial bonding with the matrix material and material degradation resulting from the recycling process. The relatively better performance of the sized recycled fibres highlights the importance of appropriate treatment and modification techniques in enhancing the mechanical properties of recycled materials. The application of sizing can help to improve the tensile strength of recycled fibres, making them more viable for use in composite materials.

Table 4. Tensile tests results

Sample type	Tensile Strength (GPa)
Reference	3.45 ± 0.41

Recycled (plasma solvolysed)	2.71 ± 0.32
Sized Recycled	3.12 ± 0.28

Conclusions

In this work, the effect of solvolysis process was investigated on carbon fibre's morphology and properties with standard characterisation techniques such as SEM, TGA and tensile tests; though special focus was given on the comparison of different methodologies to analyse optical microscopy images. Each analysis method presents its advantages and limitations, making them suitable for specific image analysis scenarios. The Olympus software emerges as the fastest option, offering immediate analysis post-image capture. However, it tends to fail in images with dense or overlapping fibres. Python scripts offer rapid analysis but necessitate the determination of optimal threshold parameters for each image. ImageJ stands out as the most consistent method, implementing a step-by-step approach that ensures accuracy but demands more time investment per image analysis. Its watershed algorithm thrives in segmenting overlapped or adjacent fibres, enhancing accuracy. In conclusion, the choice of method varies depending on the specific characteristics of the images being analyzed.
Tensile tests reveal that both sized and unsized recycled fibres exhibit reduced tensile properties compared to reference fibres, as anticipated for recycled materials. However, sizing notably enhances the tensile strength of recycled fibres, with sized fibres experiencing a relatively smaller decrease. This improvement highlights the effectiveness of sizing in counteracting negative effects associated with recycling, such as fibre damage and degradation. While the plasma assisted method proved to have better efficiency on the resin removal, both processes proved to be quite efficient on the reclamation of fibres. All the above findings emphasize the significance of suitable treatment methods in increasing the performance of recycled materials, rendering them more suitable for composite reuse applications.

Acknowledgments

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